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(54) Fire-retardant foam-forming  
coating material

(57) The fire-retardant foam-forming coating material comprises an epoxy resin binder (B) and at least one substance (S) chosen from (i) additives showing an endothermic reaction at an elevated temperature with the epoxy resin and chosen from foam-forming, gas-evolving and chain-terminating additives and/or (ii) filler material (F). The binder (B) is a hydrophilic epoxide resin which is emulsifiable with water and contains a polyamine and/or poly-amidoamine curing agent and/or a polycarboxylic acid anhydride curing agent and/or contains dicyandiamide. The invention is also concerned with a fireproofing multi-layered covering (C) comprising a barrier layer sandwiched between two layers of the said fire-retardant foam-forming coating material.

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The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

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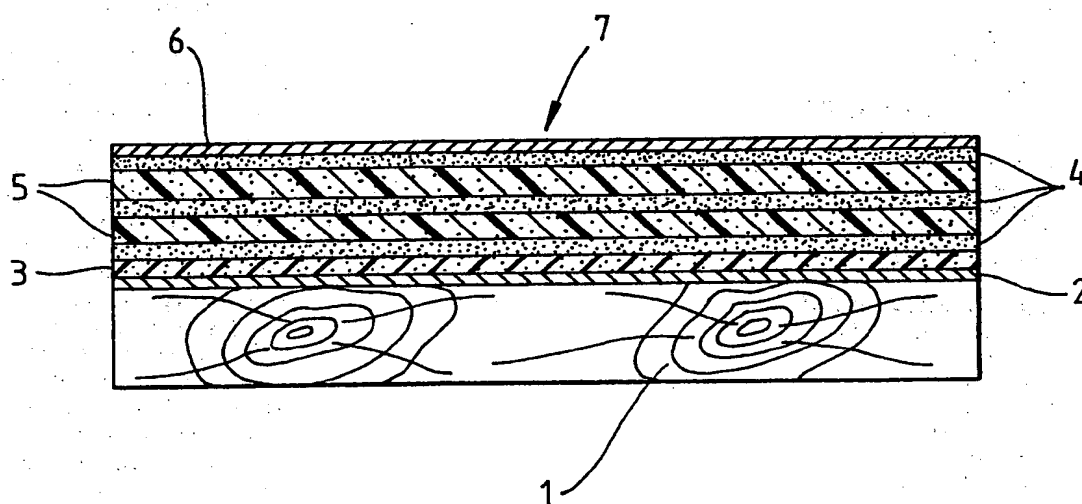


Fig. 1.

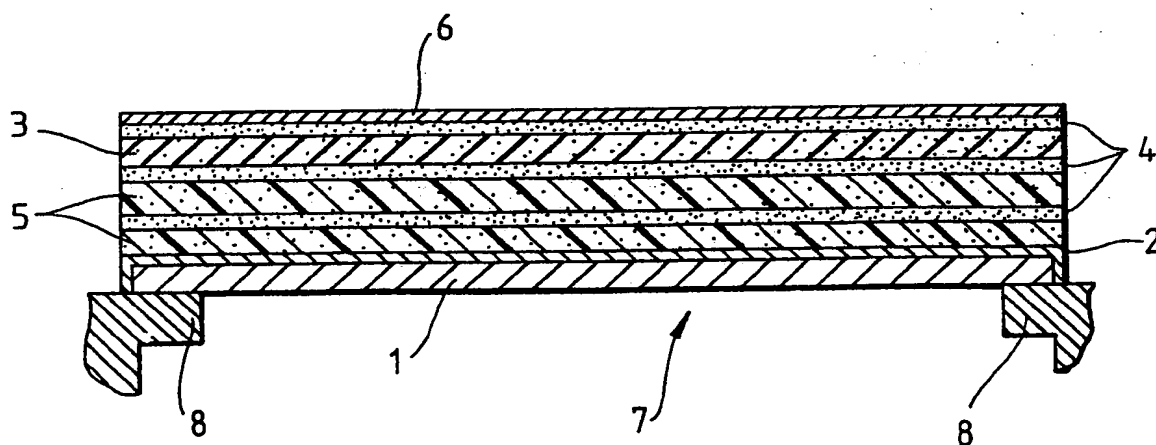


Fig. 2.

## SPECIFICATION

## Improvements in or relating to a fire-retardant foam-forming coating material

5 The present invention relates to a fire-retardant foam-forming coating material based on epoxide resin, to a fireproofed article comprising a substrate to which the said fire-retardant foam-forming coating material has been applied, to a fireproofing multi-layered covering (C) comprising a barrier layer sandwiched between two layers of the said fire-retardant foam-forming coating material, to a fireproofed article comprising a substrate to which the said fireproofing multi-layered covering (C) has been applied, to a process for  
 10 applying the said fire-retardant foam-forming coating material to a substrate and to a coated substrate so produced.

Epoxide resin materials containing, in addition to the epoxide resin, compounds of phosphoric acid or nitrogen compounds or both and additionally, if appropriate, also blowing agents, such as starch or pentaerythritol, are in themselves known. The function of the fire-retardant additives consists in producing,  
 15 when heated, a foam structure which has a heat-insulating effect, particularly if the foam structure has been carbonised. If the additives contain more than 20 mol % of nitrogen and/or phosphorus, decompose at temperatures from 100 to 400°C and are present in a quantity of 30 to 70% by weight, relative to the weight of epoxide resin and curing agent, gaseous nitrogen and fire-retardant phosphorus compounds are liberated on heating, which makes it possible to produce particularly advantageous fire-retardant protective coatings.

20 Materials of this type are disclosed in German Offenlegungsschrift 2 704 275.

Other attempts to impart a fire-retardant finish to epoxide resin materials consist in the addition of antimony compounds, phosphorus compounds, boron compounds, compounds which evolve chlorine or bromine, organic tin salts and salts of calcium, cadmium, lead, magnesium and ammonium. However it has become clear that, if these substances are used on their own or in combination, it is not possible to achieve  
 25 fire protection for an adequate period, especially in the case of buildings or other structures which must be protected from fire. In particular, values of the category F 30 according to Fire Protection Standard DIN 4102 are only achieved with difficulty using supplementary heating. These epoxide resin materials crack open prematurely on the surface, particularly if supplementary heating in an oven for small conflagrations is used, and deep cracks are formed, through which the heat rapidly reaches the article or the substrate which is  
 30 intended to be protected. A similar effect is already achieved as a result of the supplementary heating.

It has been found that certain epoxide resins which can be emulsified with water are capable, when used as binders in mixtures of this type, of firmly binding water for a relatively long time and only releasing it gradually and that, if such coatings are used on substrates, when heat is applied these coatings at the most  
 35 flake off in skin-like layers, each of which has in itself a fire-retardant action, so that altogether a very good long-term protection against the effects of fire can be achieved. This action is improved further if coatings of this type are used alternately with fibre coatings of fleece layers and, if appropriate, one or more layers of non-hydrophilic epoxide resins containing the conventional curing agents; accelerators, gas-evolving substances and/or fire-proof fillers in any desired sequence and also, if appropriate, with a final, impermeable protective layer, for example a layer of polyurethane resin, polyacrylate resin or other covering  
 40 resins which are compatible with epoxide.

According to one aspect of the invention we provide a fire-retardant foam-forming coating material comprising at least one substance (S) and an epoxy resin binder (B) therefor, the substance(s) (S) chosen from (i) additives showing an endothermic reaction at an elevated temperature with the epoxy resin and chosen from foam-forming, gas-evolving and chain-terminating additives and/or (ii) filler material (F), and  
 45 the binder (B) being a hydrophilic epoxide resin which is emulsifiable with water and contains a polyamine and/or polyamidoamine curing agent and/or a polycarboxylic acid anhydride curing agent and/or contains dicyandiamide.

Hydrophilic epoxide resins of this type are in themselves known from German Offenlegungsschrift 2 726 269, but are there merely described as anti-corrosion agents and are not described in terms of the fire  
 50 protection properties which these binders, which are emulsifiable with water, impart, particularly, in combination with the fire-proofing or fire-retardant materials which are also known, to substrates, buildings, components or parts of other structures which must be protected from fire.

In accordance with a preferred embodiment, an hydrophilic epoxide resin binder (B) is in the form of an aqueous emulsion of the hydrophilic epoxide resin and 1 to 40% by weight of water based on the total  
 55 quantity of emulsion. It is also preferable for the aqueous emulsion to contain also at least one organic emulsion stabiliser compatible with water and epoxide. The hydrophilic epoxide resin preferably contains epichlorohydrin together with bisphenol A and/or bisphenol F (2,2' - methylene diphenol). It is also preferable for the hydrophilic epoxide resin to contain an epichlorohydrin having an epoxy equivalent of 175 to 210 and a diglycidyl or triglycidyl ether of a diols or triol having 2 to 20 C atoms and, optionally 1 to 8 ether  
 60 oxygen atoms, in a weight ratio of 75 to 95% of the said epoxide resin to 25 to 5% of glycidyl ether. The amine curing agent used is preferably an adduct formed from a polyamine or polyamidoamine containing at least two amino groups, and an epoxide compound.

In accordance with a further preferred embodiment, the binder (B) contains a cycloaliphatic or aromatic carboxylic acid anhydride which reacts at temperatures between 100 and 300°C, but preferably up to 250°C,  
 65 with the epoxide resin. Substances of this type are known as curing agents and include, inter alia,

hexahydrophthalic anhydride, methylnadic anhydride, het anhydride, trimellitic anhydride and pyromellitic dianhydride. The last three substances mentioned in particular react with conventional epoxide resins at temperatures between 160 and 290°C and produce particularly heat-resistant materials.

It is also preferable to use one or more additives (i) which contain nitrogen, phosphorus, sulphur and/or bromine and decompose at 100 to 600°C as foam-forming and/or gas-evolving additives. Examples of such substances are melamine phosphate, melamine borate, guanidine phosphate, guanylurea, guanylurea phosphate, N-phenyl-N-cyclohexyl-p-phenyldenediamine, guanidine carbonate, benzosulphohydrazide, other organic sulphur compounds and bromine compounds which contain more than 10% of bromine. It is particularly preferable that the coating agent should contain 30 to 70% by weight of such substances, the quantity of nitrogen and/or phosphorus being more than 20 mol % and the decomposition temperatures being at least 50°C apart if at least two of these substances are present.

In accordance with a preferred embodiment, it is also possible to employ, as water-soluble, foam-forming additive(s), a dicyandiamide-phosphate condensation product and/or a dicyandiamide and/or guanidine silicate.

If, in addition to the binder (B), the coating material also contains a novolac resin in a quantity of 10-40% by weight, relative to the epoxide resin, particularly advantageous long-term fire protection values are obtained. A further improvement is achieved by adding one or more blowing agents, such as, preferably water-soluble, alkali metal silicates and/or meta-silicates, aluminium phosphate, aluminium oxide trihydrate and/or antimony trioxide. In this case it is possible to obtain, with supplementary heating, values up to F 90 as specified in DIN 4102, which is a value which cannot be achieved for conventional fire-retardant synthetic resins. It has also proved particularly suitable if the binder (B) contains at least one resin modified with at least one phenolic resin or contains at least one phenolic resin.

It is possible, in addition, to add to the coating material of the invention, at least one stabiliser and/or at least one further gas-evolving agent chosen from, pentaerythritol, melamine, tylose or dioxane, and also, in the case of component(s) which must be particularly protected, to add, in addition, fibres made from glass, gypsum, asbestos, graphite, boron, tungsten, steel or another heat-resistant material as filler material (F). The carbon skeleton formed under the influence of fire is mechanically stabilised as the result of additives of this type.

In accordance with a further preferred embodiment, the coating material contains 1 to 40% preferably 1 to 30% by weight, relative to the total quantity of the coating material, of diphenyl cresyl phosphate as a plasticiser and flame-retardant.

According to a second aspect of the invention there is provided a fireproofed article comprising a substrate to which the fire-retardant foam-forming coating material defined by the first aspect of the invention has been applied.

According to a third aspect of the invention there is provided a fireproofing multi-layered covering (C) comprising a barrier layer sandwiched between two layers of the said fire-retardant foam-forming material defined by the first aspect of the invention.

In use, the epoxide resin coating material of the invention may either be applied in the form of an emulsion directly to a substrate to be protected, or may first be processed independently, using a loose carrier material, and is applied at a later time to the substrate or the article which is to be protected against fire. If several layers are combined, it is possible to achieve fire protection values as specified in DIN 4102 of up to 150 minutes (without supplementary heating). Since the coating material of the invention is usually chemically neutral and is also resistant to the action of water, heat or cold, it can be used both in interior spaces and in external spaces. A particular use for the epoxide resin coating material of the invention is the protection of steel frame structures, hangars, multi-storey buildings, bridges, refineries, oil fields, pipe platforms and other articles or structures which must be protected from fire. Furthermore, it is also particularly useful for protecting structures made of wood and plastics, such as ferries or ships.

When application is made, the article to be protected is preferably first provided with a primer which depends on the article or the underlying substrate, for example, in the case of steel, a primer based on epoxide. The epoxide resin coating material of the invention may then be applied in several layers by brushing, rolling or spraying, excellent fire protection values being obtained, as a rule, from only 2 to 3 layers of 900 g/m<sup>2</sup> each. Although the thickness applied may only be 1 to 2 mm, on heating, the material expands up to 20 cm. The carbon skeleton formed in the event of fire can be stabilised by putting, between each layer, a mechanical or other barrier layer composed of fibres or fleeces which are either processed to form a fabric or are sprayed on and which are either applied in a dry state or are sprayed on wet in a single operation together with the epoxide resin coating material of the invention. All the fibres resistant to high temperatures which have previously been mentioned can be used as the fibres. However, it is also possible to use the expanding silicates previously mentioned and other hydratable metal salts of aluminium, lead, tin, boron or phosphorus. It is particularly advantageous to use aluminium phosphate or aluminium oxide trihydrate or other agents which have a strong water-binding action and only release water at elevated temperatures, such as zeolites and/or kieselguhr. The use of organic pyrolytic materials which evolve water, agents which simultaneously increase carbonisation and/or active charcoal is particularly advantageous. Under the influence of fire, the barrier layers of hydratable substances produce stable, expanded layers as a result of the evaporation of the water contained in the epoxide resin material. In addition, they have a strongly endothermic action, so that cooling of the intermediate layer is effected.

If desired, it is also possible to apply, over the two or three, or if necessary more, layers of epoxide resin coating material, a top layer which is compatible with epoxides, particularly a layer resistant to the effects of weathering and composed of polyurethane or an acrylate dispersion or another plastics material. A preferred covering (C) includes at least two barrier layers, one of the barrier layers being coated with a top layer, the top layer preferably containing an epoxide and/or a polyurethane.

In use, it is also possible to employ, besides the epoxide resin coating material of the invention, a conventional, non-hydratable epoxide resin material, the latter being applied as a second or third layer in combination with the coating material of the invention. Here too, it is possible to use intermediate layers, as described above. As a result of this it is unnecessary in many cases to apply a top layer, since the outer epoxide resin does not contain water and is thus resistant to weathering.

A preferred covering includes an additional layer which contains a non-hydrophilic or non-hydratable epoxide resin, the additional layer being attached to a layer of the said fire-retardant foam-forming material via a barrier layer.

With regard to the covering (C), the or each barrier layer may contain fibres and/or at least one organic substance or glass-like constituent which distends under hot conditions. The or each barrier layer and/or the said fire-retardant foam-forming layer may contain at least one organic, pyrolytic, water-evolving substance and/or starch, which increase(s) carbonisation. Desirably the or each barrier layer and/or the said fire-retardant foam-forming layers may contain at least one acrylonitrile butadiene or other plastics material.

A fireproofing layered element is already known (German Offenlegungsschrift No. 2 828 839); in that text a polyester/glass fibre layer is coated on both sides with a gel coat which also contains, in addition to polyester resin, other fillers and/or additives, such as melamine, pentaerythritol, potato starch and ammonium phosphate. It is also known to prepare a layered element by using an epoxide resin containing a polyamine as the curing agent. The use of glass reinforcing layers is also known. Fireproofing layered elements of this type are used, above all, for protecting buildings or parts of buildings. They contain glass fibres or metal fibres as a reinforcement. However, their fireproofing properties often do not satisfy the high requirements which are set.

In addition, it is known to use, for protecting steel components of large surface from corrosion, an aqueous epoxide resin emulsion consisting of the liquid epoxide resin based on bisphenol A and/or bisphenol F, of a reactive thinner based on a diglycidyl or triglycidyl ether, and of a curing agent based on an amine adduct formed from a polyamine containing at least two primary amino groups or one primary and one secondary amino group, and of an epoxide compound (German Offenlegungsschrift 2 726 269). The advantage of this anti-corrosion agent is that it can be applied direct to wet surfaces and has a good anti-corrosion effect in addition to good adhesion.

A fire-proofing covering (C) of the invention, is, however, intended to be improved in that it has excellent fireproofing properties in spite of having a simple structure and a simple mode of preparation. Thus in particular, it is also intended to achieve adequately long-term fire protection of structural components, including buildings, which must be protected from fire, particularly if supplementary heating as specified in Fire Protection Standard DIN 4102 is assumed. It is intended to avoid or minimise the disadvantages of fireproofing layered elements of this type, hitherto known, which crack open prematurely on the surface, with supplementary heating even in an oven for small conflagrations, and which then permit the rapid access of warmth or heat from outside to the structural component.

Barrier layers may contain, in particular, glass fibres and epoxide resin as a binder.

It has been found that this layer sequence, according to the invention, of different partial layers of the layered element achieves the object mentioned above in a particularly advantageous manner. Because the actual foam-forming layers are separated or at least covered on one side by a barrier layer, the F 30 values of DIN 4102 with supplementary heating are easily achieved. The formation of deep cracks, penetrating through the multi-layered covering (C), is prevented, and this not only when supplementary heating is applied, but also in the event of fire. In addition to good mechanical properties, exceptionally high fire protection values of up to 160 minutes as specified in DIN 4102, without supplementary heating, are achieved. A further advantage is that the fireproofing covering (C) can be used, not only in internal spaces, but also externally, and the good fireproofing properties are not lost in spite of the action of water, heat and cold. Thus values of up to F 90, with supplementary heating, have been achieved, even when used externally.

The fireproofing covering (C) according to the invention can be used with excellent results for the protection of steel frame structures, hangars, multi-storey buildings, bridges, refineries of oil fields or pipe platforms. The protection of wooden and plastic structural elements, including ships and ferries, is also ensured, in spite of the element being simple to apply.

In this respect it is appropriate, in accordance with a further development of the invention, if the covering (C) element is combined with the structural element to be protected, to form a building component; it is advisable in this case to coat the structural element with a protective layer before it is combined with the covering (C).

The covering (C) according to the invention provides good protection, that is to say good retardation of flame both in the case of radiated heat and in the case of convected heat; a stable, continuous "skin" is formed up to temperatures of about 1,000°C; if this temperature is exceeded the layer disintegrates by a surprisingly slow flaking off of thin layer sections or "skins", that is to say good long-term protection in the

heat evolved in the event of fire is also ensured.

By incorporating epoxide/phenolic resin emulsions, such as the "Beckopox" resin VEM 2155 made by Hoechst, for protection against corrosion and for increasing carbonisation, it is possible to obtain values of up to F 90 as specified in DIN 4102, with supplementary heating, which is a value which cannot be achieved for conventional fire-retardant synthetic resins.

It is also possible to use mixtures consisting of flame-retardant epoxide resins which can be emulsified in water together with mixtures consisting of flame-retardant epoxide resins which cannot be emulsified.

A covering (C) of the type described above in which the or each barrier layer and/or the said foam-forming layers contain plastics, in particular thermoplastics, such as acrylonitrile-butadiene, has proved particularly suitable.

According to a further aspect of the invention there is provided a process for applying a fire-retardant foam-forming material as defined by the first aspect of the invention to a substrate, comprising mixing one component containing a hydrophilic epoxide resin binder (B) emulsifiable with water with another component containing a polyamine and/or polyamidoamine curing agent and/or a polycarboxylic acid anhydride curing agent in the presence of at least one substance (S) chosen from (i) additives showing an endothermic reaction at an elevated temperature with the epoxy resin and chosen from foam-forming, gas-evolving and chain-terminating additives and/or (ii) filler material (F) and applying the resultant mixture to a substrate in the form of a layer and consolidating the layer.

Prior to mixing the said two components one or both of the components may be provided with at least one said substance (S) and/or filler material (F). After mixing the said two components glass fibre or other non-foaming filler material may be added thereto and the mixture applied to the substrate.

Two particularly preferred illustrative examples of a covering (C) embodying the invention are described in greater detail in the following text by means of the accompanying drawings.

Figure 1 shows a fireproofing multi-layered element which has been combined with a structural element consisting of wood to form one form of building component 7, and

Figure 2 shows an alternative fireproofing multi-layered element which has been combined with a structural element consisting of sheet metal, to form a second form of building component 7.

In accordance with Figure 1, the structural element 1, which is constructed in the form of a wooden beam, has been coated with a protective layer 2. To the protective layer 2 an additional layer 3 has been applied, on which a barrier layer 4, and over that a fire-retardant foam-forming layer 5, and over that a barrier layer 4, and over a second fire-retardant foam-forming layer 5, and over that a further barrier layer 4 and finally a top layer 6, have been built up.

The composition of the individual component layers is described further in the following text.

In accordance with Figure 2, a metal sheet 1 which has also been coated with a protective layer 2 on its external faces and on both front faces, is used as the structural element. This component has been combined with a fireproofing multi-layered element to form a building component and can, therefore, be transported as a building component and can be assembled to form a complete covering of articles to be protected. In this case one of the fire-retardant foam-forming layers 5 is adjacent to the protective layer 2 and the additional layer 3 is located next to a barrier layer 4 which has been introduced between this additional layer 3 and the other of the foam-forming layers 5. Here too, the external barrier layer 4 has been covered with a top layer 6. This building component is set up upon supports 8, for example supporting walls or supporting columns, and it can be anchored there in a suitable manner.

The multi-layered element can be produced in various ways, particularly by building up the individual layers in stages, by first coating the structural element 1 with the protective layer, in particular an adhesive primer, an anti-corrosion layer or a similar primer. If the structural element 1 is composed of steel, it is advisable to prepare the protective layer 2 by using epoxide resin. On heating, the multi-layered element expands, by means of the fire-retardant foam-forming layers, by a factor of 10 to 100, for example up to 20 cm. Because a mechanical barrier layer 4 consisting of fibres, fleeces, fabrics and the like has been inserted between each fire-retardant foam-forming layer 5, the carbon skeleton formed in a fire is stabilised. The fibres can be blown on; they can also be sprayed on in a dry state or even in a wet state in a single operation, together with the epoxide resin coating material.

The barrier layers not only provide mechanical stabilisation, but, if subjected to fire or heat, produce stable, expanded layers as a result of the evaporation of the water contained in the epoxide resin. They also produce a strongly endothermic effect, so that cooling takes place at the same time.

The top layer 6 should appropriately be compatible with epoxide and should be resistant to the effects of weathering. The use of polyurethane or an acrylate dispersion is recommended for this purpose.

The following composition of the layers is particularly preferred:

The protective layer 2 used is a primer based on epoxide resins, on a steel structure serving as the structural element 1, this primer being applied in a very thin layer to the structural element 1 in Figure 2.

For the foam-forming layers 5, the following components are used, A as the binder and B as the curing agent.

## Parts by Weight

5	A) Hydratable epoxide resins formed from bisphenol A and epichlorohydrin, epoxide number 24-25, epoxide equivalent 172-178, Gardner Colour No. 1-3, density 1.13 (20°C), viscosity 1,200-1,500 cP (Rütapox VE 2913)	22	5
10	Novolac resin, 80% strength acrylate dispersion (4186 Rütgerswerke) or a dispersion of an acrylate modified epoxide resin, such as VEM 37/1 (Hoechst)	5.0	10
	Stabiliser (VVE, Rütgerwerke Duisburg) (optionally tylose (MHB 10,000, Hoechst AG)	1.2	
15	Pentaerythritol	9.0	15
	Melamine resin (Maprenal VMF 3910)	5.0	
	Phosphate flame-retardant (Phoscheck P 30)	13.0	
20	Titanium dioxide	9.9	20
	Tris-(dichloroethyl) phosphate containing emulsifiers (Phosgard C22R)	6.5	
25	Milled glass fibres (Milled Fiber EC-10S)	2.4	25
	Distilled Water	20.0	
30			30
	B) Polyamine curing agent, amine equivalent 125-150, viscosity 7,000-8,000 cP, density 1.0 (20°C), Gardner Colour 8-10, 75% solids content (Rütgerswerke AB S4 or H 553)	53.6	
35	Amidoamide curing agent (105/B, Rütgerswerke)	26.8	35
	Anhydride curing agent (Y. Rütgerswerke)	7.9	
	Guanylurea	10.0	
40	Trisdimethylaminophenol (DMP 30)	10.7	40

45 An aqueous emulsion is prepared from five parts of the component A and one part of the component B and the first foam-former layer 5 is then applied. The pot life is 2 hours, so that 1 to 2 days elapse, for a multi-layer coating, until the next layer can be applied.

The first barrier layer 4 is then applied to the first, in this case the lowest or innermost fire-retardant foam-forming layer 5, either wet on wet or in a dry condition, using glass fibres, and in such a manner that a layer 5, about 100 to 300 µm thick, is first applied and the glass fibres, cut into lengths of 4-20 mm, in particular 6 mm, are then sprayed on by means of glass-chopping equipment, using a current of air, or by means of a resin spraying device.

55 A particularly advantageous process illustrating the process of the invention consists in initially preheating firstly the emulsifiable epoxide resin, to which one or more additives (i) and/or filler material (F) has/have already been added, in the form of a slightly doughy composition and, secondly, the curing agent - in the form of a pasty composition to which the additive(s) (i) and/or filler material (F) has/have also been added - in order to reduce viscosity thereof and/or to improve flow thereof. The components, having a viscosity which has thus been reduced to about 10% or less, are then mixed under a high injection pressure of about 200 to 300 bars in a static mixer in which the volume stream of each individual component is divided many times and excellent mixing thus takes place even without dynamic treatment. The mixing ratio can be controlled at the same time. However, it is advisable to have a ratio of about 4:1 between the emulsifiable epoxide resin into which additives have been incorporated, for example as specified in component A, and the curing agent which has the composition specified for component B.

60 After mixing, the mixture is again split into two individual jets in order to coat finely chopped up glass fibres within the showering range of a spray gun, and in order to be sprayed as coating layers onto the object to be protected, for example the wall of a safe or a piece of armour plate.

The total layer thickness is about 0.6 to 1.5 mm. The next fire-retardant foam-forming layer 5 is then applied in a similar manner, as indicated above. After the next barrier layer 4 has been built up, one or more additional layers 3 are built up, these being composed of a mixture of 4 parts by weight of the component E and 1 part by weight of the component F, as formulated below:

5		Parts by weight	5
	E) Epoxide resin formed from bisphenol A and epichlorohydrin (non-hydratable) (Beckepox EP 117, Hoechst AG)	29.0	
10	Novolac resin (VS 4186, 80% strength, Rütgerswerke)	11.5	10
	Pentaerythritol	12.0	
15	Phoscheck P 30	18.0	15
	Melamine resin (Maprenal MF 980)	3.5	
	Titanium dioxide	8.4	
20	Tris-(dichloroethyl) phosphate	9.3	20
	Melamine resin (Maprenal MF 590)	6.5	
25	Glass fibre (milled fiber EC-105)	1.8	25
	F) Amine curing agent (Euredur 43, Hoescht AG)	40.8	
30	Amine curing agent (LC, Rütgerswerke)	25.4	30
	Anhydride curing Agent (Y, Rütgerswerke)	7.7	
	Trisdimethylaminophenol (DMP 30)	7.7	
35	Asbestos fibres (Sylodex 2X)	1.1	35
	Guanylurea	15.4	
40	Glass fibre (milled fiber EC 105)	1.9	40

The pot life of this mixture of components is 40 minutes; the mixing ratio of E and F = 4:1.

After a further barrier layer 4 has been built up, the top layer 6 is finally applied; this, in turn, consists of 45 parts of the component C and one part of the component D as specified in the following mixture:

45



## Parts by Weight

5	C) Polyester formed from adipic acid, phthalic acid, triol and diol 80% strength in ethylglycol acetate (VPKL 5 2332, Bayer AG)	39.14	5
	Titanium dioxide	27.48	
10	Montmorillonite/alkylammonium salt thickener (Bentone 34), 10% strength in benzene	5.44	10
	Zinc accelerator (Nuvofox, 8% of Zn)	0.11	
15	Silicone oil (OL, 10% strength)	0.530	15
	Tris-(dichloroethyl) phosphate	7.7	
	Aluminium oxide trihydrate	7.7	
20	Ethylglycol acetate	4.37	20
	Butylglycol acetate	7.6	
25	D) Mixture of aromatic diisocyanates (Desmodur VPKL, Bayer AG)		25
30	Mixing ratio of C : D = 4:1. The resulting material had a flame-retardation value of 150 minutes as specified in DIN 4102. In order to prevent the layers shrinking when cured, plasticiser is added to all the layers, specifically, if appropriate, dicresyl phenyl phosphate in quantities of 2-10% relative to the particular formulation. It is possible to mix the component A of the emulsifiable resin with the component E of the non-emulsifiable resin to obtain maximum effect; this is done in a ratio of A:E of 10 to 60:90 to 40.		30
35	In many cases it is necessary to shape the structural elements for the combination of layers before they are processed further. In this case, thin metal sheets may be used, which can be bent or folded to a varying extent. Since it is difficult to coat these metal sheets in a bent state, it is advantageous to coat the metal sheets in a flat state by hand or mechanically. In a mechanical process, the individual layers can be applied successively on a conveyor belt, and a curing zone employing hot air or infrared radiation can be interposed between the layers. This makes it possible to set a conveyor belt speed of 20-90 m/minute. The formulation should, however, be modified for bending, since the layers should be formulated so as to be similar to rubber. This is best effected by adding 10 to 40% of bicresyl phenyl phosphate and/or thermoplastics. Homopolymers of butadiene and butadiene/acrylonitrile copolymers containing reactive groups in both terminal positions have proved particularly suitable. These reactive groups can be carboxyl, hydroxyl, vinyl and also amino end groups. In the present example, the curing agents B or the curing agents F can be mixed with a product containing amino end groups, for example HYCAR ATBN-1300 X 6 (B.F. Goodrich).		35
40			40
45			45
50	Viscosity, cP Brookfield	225,000	50
	Total amine equivalent	800-1,000	
55	Acrylonitrile content	16.5	55
	Specific gravity at 25°C	0.956.	
60	For example, 60 parts by weight of HYCAR ATBN are added to the curing agent B. The mixing ratio in the example is then altered as follows:		60

$$A:B = 2.5:1$$

60 parts by weight of HYCAR ATBN are also added to the curing agent F, and the mixing ratio is then altered to:

$$E:F = 2:1$$

5

After curing, elastic layers are formed, which exhibit no cracks on their edges when bent.

Acrylonitrile - and/or butadiene homopolymers can also be added to the epoxide resin itself instead of to the curing agent.

This is effected by mixing the carboxyl-containing acrylonitrile or butadiene copolymers with the epoxide resins and processing the mixture at an elevated temperature.

#### Example:

15

Epoxide resin of Example E

100 g

HYCAR 1300 XB RLP

20 g

Processing is carried out at about 130°C for approximately 16 hours.

While the preparation is still liquid, 40 parts by weight are introduced into the composition E.

It is also possible, in addition, to use the curing agent F, modified with HYCAR.

In addition to use for bent or folded metal sheets, advantages of further fireproofing result, because the preparation with a high N content have an additional flame-retardant action in the carbonisation process. The content of homopolymers results in even better prevention of shrinking, so that in the event of fire no

micro-cracks are formed and the action of the plasticisers, such as diphenyl cresyl phosphate, is reinforced.

As a rule, the fire-retarding protective elements are indeed applied in the form of a fire-proofing layer to an article which is to be protected, for example the wall of a safe, a piece of armour plate or a structural element, such as an aircraft component or a building structure. However, it is also possible to produce the protective element in the form of an independent and particularly pliable component, in order to put it in the desired position only when it is in the site where it will be used. In this respect the invention can be applied in a very versatile manner.

#### CLAIMS

1. A fire-retardant foam-forming coating material comprising at least one substance (S) and an epoxy resin binder (B) therefore the substance(s) (S) chosen from (i) additives showing an endothermic reaction at an elevated temperature with the epoxy resin and chosen from foam-forming, gas-evolving and chain-terminating additives and/or (ii) filler material (F), and the binder (B) being a hydrophilic epoxide resin which is emulsifiable with water and contains a polyamine and/or polyamidoamine curing agent and/or a polycarboxylic acid anhydride curing agent and/or contains dicyandiamide.

2. A coating material according to claim 1, wherein the hydrophilic epoxide resin binder (B) is in the form of an aqueous emulsion of the hydrophilic epoxide resin and 1 to 40% by weight of water based on the total quantity of emulsion.

3. A coating material according to claim 2, wherein the aqueous emulsion contains at least one organic emulsion stabilizer compatible with water and epoxide.

4. A coating material according to claim 2 or claim 3, wherein the hydrophilic epoxide resin contains epichlorohydrin together with bisphenol F and/or bisphenol A.

5. A coating material according to claim 4, wherein the hydrophilic epoxide resin contains an epichlorohydrin having an epoxy equivalent of 175 to 210 and a diglycidyl or triglycidyl ether of a diol or triol having 2 to 20 carbon atoms and, optionally 1 to 8 ether oxygen atoms, in a weight ratio of 75 to 95% of the said epoxide resin to 25 to 5% of glycidyl ether.

6. A coating material according to any preceding claim, wherein the binder (B) contains an amine curing agent constituted by an adduct formed from a polyamine or polyamidoamine having at least two amino groups.

7. A coating material according to any one of the preceding claims, wherein the binder (B) contains a cycloaliphatic or aromatic carboxylic acid anhydride which reacts with the epoxide resin at temperatures between 100 and 300°C.

8. A coating material according to any one of the preceding claims, wherein the additives (i) contain nitrogen and/or phosphorus and decompose at temperatures between 100 and 600°C.

9. A coating material according to claim 8, wherein between 30 and 70% by weight (calculated on the total weight of the coating material) of at least one substance (S) chosen from additives (i) which contain more than 20 mol % of nitrogen and/or phosphorus is present.

10. A coating material according to claim 9, wherein at least two of these additives (i) as defined in claim 9 are used, their decomposition temperatures differing from one another by at least 50°C.

11. A coating material according to claim 9, wherein at least two of the following additives (i) are present:

melamine phosphate, melamine borate, guanidine phosphate, guanylurea, guanylurea phosphate, N-phenyl-N-cyclohexyl-p-phenylenediamine, guanidine carbonate, benzosulphohydrazide, other organic sulphur compounds and bromine compounds which contain more than 10% of bromine.

12. A coating material according to any one of the preceding claims, wherein there is present a dicyandiamide-phosphate condensation product and/or a dicyandiamide and/or a guanidine silicate as water-soluble, foam-forming additive(s). 5
13. A coating material according to any one of the preceding claims, wherein there is present at least one additive chosen from an alkali metal silicate, an alkali metal metasilicate, aluminium phosphate, aluminium oxide trihydrate, antimony trioxide, a zeolite, kieselguhr, starch, pentaerythritol and substances which simultaneously increase carbonisation, and substantially pure active charcoal as foam-forming and/or flame-retardant additive(s). 10
14. A coating material according to any one of the preceding claims, wherein there is present at least one additive chosen from a melamine, tylose and dioxane as an additional stabiliser and/or gas-evolving agent.
15. A coating material according to any one of the preceding claims, wherein the binder (B) is an epoxide resin containing a novolac resin in a proportion of 10 to 40% by weight of novolac resin relative to the epoxide resin. 15
16. A coating material according to any one of the preceding claims, wherein the binder (B) contains at least one resin modified with at least one phenolic resin or contains at least one phenolic resin.
17. A coating material according to any one of the preceding claims, wherein there are present fibres made of glass, gypsum, asbestos, graphite, boron, tungsten, steel and/or other heat-resistant materials are used as filler material (F). 20
18. A coating material according to any one of the preceding claims, which includes 1 to 40% by weight relative to the total quantity of the coating material of diphenyl cresyl phosphate as a plasticiser and flame-retardant.
19. A fire-retardant foam-forming coating material according to claim 1 substantially as herein described and exemplified. 25
20. A fireproofed article comprising a substrate to which the fire-retardant foam-forming coating material claimed in any preceding claim has been applied.
21. A fireproofing multi-layered covering (C) comprising a barrier layer sandwiched between two layers of the said fire-retardant foam-forming coating material claimed in any one of claims 1 to 19. 30
22. A covering (C) according to claim 21, including at least two barrier layers, one of the barrier layers being coated with a top layer.
23. A covering (C) according to claim 22, wherein the top layer contains an epoxide and/or a polyurethane.
24. A covering (C) according to any one of claims 21 to 23, which includes an additional layer which contains a non-hydrophilic or non-hydratable epoxide resin, the additional layer being attached to a layer of the said fire-retardant foam-forming material via a barrier layer. 35
25. A covering (C) according to any one of claims 21 to 24, wherein the or each barrier layer contains fibres and/or at least one organic substance or glass-like constituent which distends under hot conditions.
26. A covering (C) according to any one of claims 21 to 25, wherein the or each barrier layer and/or the said fire-retardant foam-forming layer contain(s) at least one organic, pyrolytic, water-evolving substance and/or starch, which increase(s) carbonisation. 40
27. A covering (C) according to any one of claims 21 to 26, wherein the or each barrier layer and/or the said fire-retardant foam-forming layers contain(s) at least one acrylonitrile butadiene or other plastics material. 45
28. A covering (C) according to claim 21 substantially as herein described and exemplified and/or with reference to Figure 1 or Figure 2 of the accompanying drawings.
29. A fireproofed article comprising a substrate to which the fireproofing multi-layered covering (C) claimed in any one of claims 21 to 28 has been applied.
30. A fireproofed article according to claim 29, in which a protective layer has been applied to the substrate and is sandwiched between the substrate and the covering (C). 50
31. A process for applying a fire-retardant foam-forming coating material as claimed in any one of claims 1 to 19 to a substrate, comprising mixing one component containing a hydrophilic epoxide resin binder (B) emulsifiable with water with another component containing a polyamine and/or polyamidoamine curing agent and/or a polycarboxylic acid anhydride curing agent in the presence of at least one substance (S) chosen from (i) additives showing an endothermic reaction at an elevated temperature with the epoxy resin and chosen from foam-forming, gas-evolving and chain-terminating additives and/or (ii) filler material (F) and applying the resultant mixture to a substrate in the form of a layer and consolidating the layer. 55
32. A process according to claim 31, wherein prior to mixing the said two components one or both of the components is provided with at least one said substance (S) and/or filler material (F). 60
33. A process according to claim 31 or claim 32, wherein after mixing the said two components glass fibre or other non-foaming filler material is added thereto and then the mixture is applied to the substrate.
34. A process according to claim 31 substantially as herein described and exemplified.
35. A coated substrate which has been produced by the process claimed in any one of claims 31 to 34.

New claims or amendments to claims filed on 14 May 1981

Superseded claims 1 and 31

New or amended claims

- 5 1. A fire-retardant foam-forming coating material comprising at least one substance (S) and an epoxy resin binder (B) therefore the substance(s) (S) chosen from (i) additives showing an endothermic reaction at an elevated temperature with the epoxy resin and chosen from foam-forming, gas-evolving and/or chain-terminating additives and/or (ii) filler material (F), and the binder (B) being a hydrophilic epoxide resin which is emulsifiable with water and contains a polyamine and/or polyamidoamine curing agent and/or a polycarboxylic acid anhydride curing agent and/or contains dicyandiamide. 5
- 10 31. A process for applying a fire-retardant foam-forming coating material as claimed in any one of claims 1 to 19 to a substrate, comprising mixing one component containing a hydrophilic epoxide resin binder (B) emulsifiable with water with another component containing a polyamine and/or polyamidoamine curing agent and/or a polycarboxylic acid anhydride curing agent in the presence of at least one substance (S) 10
- 15 chosen from (i) additives showing an endothermic reaction at an elevated temperature with an epoxy resin and chosen from foam-forming, gas-evolving and/or chain-terminating additives and/or (ii) filler material (F) and applying the resultant mixture to a substrate in the form of a layer and consolidating the layer. 15